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Heteropolymetallic complexes containing ReO_4^-: Catalytic oxidation of sulfide

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ABSTRACT

Heteropolymetallic complexes [(salen)Ti(ReO_4)$_2$] (**1**) and [{(salen)Ti(ReO_4)}$_2$(μ-O)] (**2**) are easily obtained in high yields *via* reaction of [(salen)$TiCl_2$] and [{(salen)$TiCl_2$}$_2$(μ-O)] with (Me_3SiO)ReO_3, respectively (where, salen = (S,S)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine dianion). The structure of complex **2** was established by single-crystal X-ray diffraction. The tetrahedral geometry of the ReO_4^- anion links the dititanium unit of {(salen)Ti}$_2$(μ-O) in the axial positions. The Re–O–Ti bridge angles range from 146.1(2) to 162.6(2) with a Re···Ti separation of 3.780 Å. Complexes **1** and **2** are capable of catalytic oxidation of sulfides with ^{t}BuOOH.

1. Introduction

Heteropolymetallic complexes have recently proven active in a number of catalytic transformations that are not accessible with analogous monometallic complexes [1,2]. Many heterometallic complexes have been prepared, including a few that show catalytic activity [3–6]. For example, the Ru–Cr complexes [Ru(N)(CH_2SiMe_3)$_2$(μ-O)$_2$$CrO_2$]$^-$ with chromate group coordinating to nitrido(dialkyl)metal center through two oxo ligands, catalyze the selective oxidation of alcohols with molecular oxygen. The hydride abstraction by a chromium oxo group is observed in the concerted β-hydrogen elimination mechanism [7]. So, it seems like that metal-oxo anions are excellent candidates for forming the heterometallic complexes.

The perrhenate group (ReO_4^-) is a weak coordinating anion, which is not only used as a couterion, but also directly coordinates other metal to form Re–O–M framework. The coordination chemistry of the perrhenate anion has received increasing attention due to their applications in catalytic organic oxidations, magnetic and supramolecular structure study. To date, the bimetallic complexes with Ag^I/Re^{VII} [8], M^{II}/Re^{VII} (M = Fe, Ni, Cu) [9–16], M^{IV}/Re^{VII} (M = Ti, Zr, U) [17–20] or Ru^{II}_2/Re^{VII} [21] have been reported. For instance, the Mn–Re complex [Mn_2(saltmen)$_2$(ReO_4)$_2$] (saltmen^{2-} = *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)) unambiguously exhibits single-molecule magnetic behavior [22]. The Cu–Re complexes [Cu(pc)(ReO_4)] and [Cu(pc)(ReO_4)$_2$] (pc = phthalocyanine) display a localized distribution of charge, that is contrary to expected metallic conductivity [11,12].

Recently, Chaudhury groups have reported heterometallic complex [(metsalen)VO(ReO_4)]·H_2O (metsalen = *N*,*N*′-ethylene bis(salicylideneimine)), of which ReO_4^- coordinates axially to the vanadium metal centers [23]. Redox behavior of this compound indicates the reducing electron enters the V^V center and remains partially delocalized between the V^V and Re^{VII} centers. That gives an opportunity to solubilize a perrhenate anion in organic solvents for its potential use as catalyst for various oxidation reactions on organic substrates. In our research, we have found the perrhenate anion can be activated by coordination with d^0 metal center, notably Ti^{IV}, Zr^{IV}. The perrhenate group in [L_{OEt}Ti(ReO_4)$_3$] and [L_{OEt}Zr(ReO_4)$_3$(H_2O)] (where L_{OEt}^- = [CpCo{P(O)(OEt)$_2$}$_3$]$^-$) are capable of catalyzing oxidation of methyl *p*-tolyl sulfide in presence of oxidant [19]. We set out to extend heterometallic perrhenate coordination chemistry into asymmetric oxidation reaction. Herein we describe the synthesis and structural studies of heteropolymetallic complexes [(salen)Ti(ReO_4)$_2$] (**1**) and [{(salen)Ti(ReO_4)}$_2$(μ-O)] (**2**) (salen = (S,S)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine dianion) The catalytic oxidation of sulfides under ^{t}BuOOH is also reported.

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2. Experimental

2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled and degassed prior to use. ^{1}H NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz, and chemical shifts (δ, ppm) were reported with reference to $SiMe_4$. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by a PE240C elemental analyzer. The startings [(salen)$TiCl_2$] and [{(salen)TiCl}$_2$(μ-O)] were prepared according to literature methods [26]. *tert*-Butyl hydroperoxide (TBHP, 5 M in decane) and sulfides were obtained from J&K Scientific Ltd.

2.2. Synthesis of [(salen)Ti(ReO_4)$_2$] (**1**)

To a solution of (Me_3SiO)ReO_3 (138 mg, 0.43 mmol) in CH_2Cl_2 (4 mL) was added solution of [(salen)$TiCl_2$] (73 mg, 0.11 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred overnight. The solvent was removed in vacuum and the brown-red solid was washed with Et_2O (3 × 3 mL). Recrystallization from CH_2Cl_2–Et_2O–hexane (1:15:4 mL) afforded the needle brown-red crystals. Yield: 80 mg (67%). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 18H, *t*Bu), 1.56 (s, 18H, *t*Bu), 1.52–1.58 (m, 4H, –CH_2), 2.15 (m, 2H, –CH_2), 2.65 (m, 2H, –CH_2), 3.65 (m, 2H, –CH_2), 7.41 (d, J = 1.2, 2H, Ph), 7.68 (d, J = 1.2, 2H, Ph), 8.41 (s, 2H, N = CH) ppm. IR (KBr, cm^{-1}): 605(m), 658(w), 723(w), 764(m), 819(vs), 849(s), 872(s), 918(vs), 1025(w), 1183(w), 1206(w), 1248(s), 1270(m), 1298(w), 1324(w), 1361(w), 1392(w), 1440(w), 1463(w), 1558(m), 1610(s), 2868(m), 2958(s), 3442(br, w). UV–vis(CH3CN) [λ_{max}, nm (ε, mol^{-1} cm^2)]: 249 (43300), 302 (14200). *Anal.* Calc. for $C_{36}H_{52}O_{10}N_2TiRe_2 \cdot 0.5Et_2O$: C, 40.38; H, 5.08; N, 2.48. Found: C, 40.86; H, 5.27; N, 2.26%.

2.3. Synthesis of [{(salen)Ti(ReO_4)$_2$}$_2$(μ-O)] (2)

A mixture of (Me_3SiO)ReO_3 (71 mg, 0.22 mmol) and [{(salen)$TiCl_2$}$_2$(μ-O)] (127 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was stirred overnight, of which color changed from orange to darkish red. The solvent was removed in vacuum and the resulted darkish-red solid was washed with hexane. Extraction of CH_2Cl_2 was layered with Et_2O–hexane to afford single needle red crystals which were suitable for the X-ray diffraction study. Yield: 142 mg (85%). ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu), 1.35 (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu), 1.55 (m, 8H, –CH_2), 1.69 (m, 4H, –CH_2), 1.92 (m, 2H, –CH_2), 2.47 (m, 2H, –CH_2), 2.37 (m, 4H, –CH_2), 7.20 (d, J = 1.0, 2H, Ph), 7.26 (2H, Ph), 7.50 (d, J = 1.0, 2H, Ph), 7.59 (d, J = 1.0, 2H, Ph), 8.07 (s, 2H, N = CH), 8.24 (s, 2H, N = CH) ppm. IR (KBr, cm^{-1}): 551(m), 593(s), 646(m), 716(vs), 761(s), 801(s), 850(s), 917(s), 1020(s), 1097(s), 1180(m), 1202(m), 1254(vs), 1393(s), 1359(m), 1393(m), 1440(m), 1464(m), 1555(m), 1615(vs), 2864(m), 2911(m), 2959(vs), 3435(br, w). UV–vis(CH3CN) [λ_{max}, nm (ε, mol^{-1}cm^2)]: 256 (30270), 384 (9730). *Anal.* Calc. for $C_{72}H_{104}O_{13}N_4Ti_2Re_2$: C, 50.82; H, 6.16; N, 3.29. Found: C, 50.16; H, 5.85; N, 3.42%.

2.4. Catalytic oxidation of sulfides with TBHP

Typically, a mixture of sulfide (0.10 mmol), oxidant (0.50 mmol), and 1.0 mol% of catalyst (1.0 µmol) in 2 mL of CH_2Cl_2 was stirred at room temperature under nitrogen. The organic products were determined by GLC analysis using iodobenzene as internal standard.

Table 1
Crystallographic data and experimental details for complex [**2**]$_2 \cdot 4Et_2O$.

Complex	[**2**]$_2 \cdot 4Et_2O$
Formula	$C_{80}H_{124}N_4O_{15}Re_2Ti_2$
Formula weight	1850.03
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	19.9022(1)
b (Å)	17.8522(1)
c (Å)	24.9096(1)
β (°)	90.652(1)
V (Å^3)	8849.76(8)
Z	4
ρ_{calc}, (g cm$^{-3)}$	1.389
T (K)	133(2)
λ (Å)	1.5418
μ (mm^{-1})	7.174
F(000)	3784
No. of reflections	58968
No. of independent reflections	26226
R_{int}	0.0424
Goodness-of-fit (GOF)[a]	1.008
R_1[b], wR_2[c] [$I > 2\sigma(I)$]	0.0359, 0.0836
R_1, wR_2 (all data)	0.0397, 0.0849

[a] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{½}$.
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] wR_2 $[(\Sigma w|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.

Table 2
Selected bond distances (Å) and angles (°).

Re1–O11	1.738(4)	Ti1–N1	2.137(4)
Re1–O12	1.712(6)	Ti1–N2	2.128(5)
Re1–O13	1.698(7)	Ti2–O3	1.859(4)
Re1–O14	1.680(7)	Ti2–O4	1.850(4)
Re2–O15	1.776(5)	Ti2–O9	1.824(4)
Re2–O16	1.710(5)	Ti2–O15	2.105(4)
Re2–O17	1.697(5)	Ti2–N3	2.148(5)
Re2–O18	1.701(5)	Ti2–N4	2.140(5)
Re3–O19	1.756(4)	Ti3–O5	1.850(4)
Re3–O20	1.700(5)	Ti3–O6	1.852(4)
Re3–O21	1.719(6)	Ti3–O10	1.827(4)
Re3–O22	1.698(6)	Ti3–O19	2.098(4)
Re4–O23	1.750(4)	Ti3–N5	2.133(5)
Re4–O24	1.725(5)	Ti3–N6	2.140(4)
Re4–O25	1.695(6)	Ti4–O7	1.864(4)
Re4–O26	1.714(6)	Ti4–O8	1.852(4)
Ti1–O1	1.851(4)	Ti4–O10	1.804(4)
Ti1–O2	1.853(4)	Ti4–O23	2.149(4)
Ti1–O9	1.806(4)	Ti4–N7	2.132(4)
Ti1–O11	2.137(5)	Ti4–N8	2.145(5)
O12–Re1–O11	110.1(3)	O20–Re3–O19	111.0(2)
O13–Re1–O11	109.7(3)	O20–Re3–O21	108.4(3)
O13–Re1–O12	107.9(3)	O21–Re3–O19	109.4(3)
O14–Re1–O11	109.5(3)	O22–Re3–O19	109.2(3)
O14–Re1–O12	109.1(4)	O22–Re3–O20	109.6(3)
O14–Re1–O13	110.5(4)	O22–Re3–O21	109.2(3)
O16–Re2–O15	107.9(2)	O24–Re4–O23	110.1(2)
O17–Re2–O15	109.5(2)	O25–Re4–O23	110.3(2)
O17–Re2–O16	109.4(3)	O25–Re4–O24	108.9(3)
O17–Re2–O18	109.0(3)	O25–Re4–O26	108.6(4)
O18–Re2–O15	111.0(2)	O26–Re4–O23	109.3(2)
O18–Re2–O16	109.9(3)	O26–Re4–O24	109.7(3)
Ti1–O9–Ti2	170.9(3)	Ti4–O10–Ti3	166.8(2)
Re1–O11–Ti1	160.9(2)	Re3–O19–Ti3	162.6(2)
Re2–O15–Ti2	150.9(2)	Re4–O23–Ti4	146.1(2)

2.5. X-ray crystallography

Complex [**2**]$_2 \cdot 4Et_2O$ were collected on an Oxford Diffraction GeminiTMS Ultra with CCD Area Detector with monochromatized Cu-Kα radiation (λ = 1.54178 Å). Data collection and reduction were carried out using CrysAlisPro 171.32.5. Absorption correction was performed using SADABS built-in the CrysAlisPro program suite

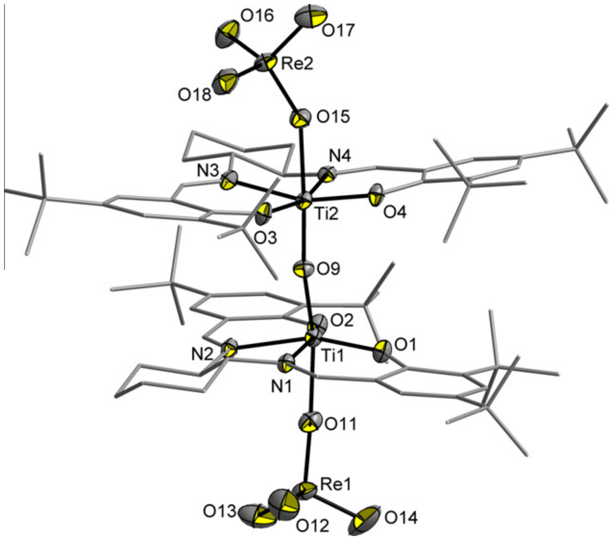


Fig. 1. The molecular structure of complex **2** (The hydrogen atoms are omitted for clarity. Probability of ellipsoids of 50% is shown).

[30]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [31]. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms. In $[\mathbf{2}]_2{\cdot}4Et_2O$, four ether molecules were co-crystallized. Two of them are disordered and refined with appropriate partial occupancies. The butyl groups of salen ligands were also found to be disordered. Carbon atoms C73, C74, C75 are 70:30 disordered, C123, C124, C125 are 50:50 disordered and C173, C174 and C175 on butyl groups are 60:40 disordered.

3. Results and discussions

No reaction happened in presence of $NaReO_4$ in the solution of $[(salen)TiCl_2]$ in CH_2Cl_2, whereas treatment of $[(salen)TiCl_2]$ with two equivalents of $AgReO_4$ led to isolation of **1** in low yield, as evidenced by NMR spectroscopy. **1** could be isolated in ca. 67% yield by treatment of excess of $(SiMe_3O)\,ReO_3$ with $[(salen)TiCl_2]$ in CH_2Cl_2. Complex **2** was obtained in ca. 85% yield under the similar procedure. The driving force of these reactions is the formation of Me_3SiCl. Complex **1** and **2** are soluble in common organic solvent such as CH_2Cl_2 and tetrahydrofuran, but insoluble in ether and hexane. The complexes **1** and **2** are medium air stable. It decomposed into brown solid after exposed in air for few weeks. The IR spectra of **1** and **2** shows a couple of strong bands at 1610, 1248 cm^{-1} (for **1**) and 1615, 1254 cm^{-1} (for **2**) regions due to the ν(C=N) and ν(C–O/phenolate) stretching modes of the coordinated Shiff base moieties, respectively. A sharp strong band at 918 cm^{-1} for **1**, and 917 cm^{-1} for **2** are observed due to the presence of ReO_4^- anion in the unidentate mode of coordination [6,13,24]. The ^1H NMR spectrum of complex **1** in $CDCl_3$ displays two singlet at δ = 1.38, 1.56 ppm due to the ^{t}Bu protons along with a singlet at δ = 8.41 ppm assignable to imino proton in the salen ligand. In complex **2**, the singlet peaks at 1.19, 1.34, 1.35 and 1.41 ppm are assigned to ^{t}Bu, and peaks at 8.07 and 8.24 ppm are attributed to imino protons.

The crystallographic data and experimental details for complex $[\mathbf{2}]_2{\cdot}4Et_2O$ are shown in Table 1. The selected bond distances and angles are listed in Table 2. The perspective view of complex **2** is displayed in Fig. 1. The complex crystallizes in a monoclinic space group $P2_1$ with two molecular units of **2** and four cocrystallized ether molecules per cell. **2** is non-centrosymmetric. The Ti^{IV} is equatorially hexa-coordinated by two O atoms and two N atoms from salen ligand, and axially coordinated with two O atoms contributed by bridged-oxo from Ti–O–Ti and O–ReO_3 fragments, respectively. Ti atoms move out of the N_2O_2 least-squares meridian plane by 0.359–0.385 Å toward the apical bridged O9 or O10 atoms, which is similar that of $[\{(salen)Ti(CH_3CO)\}_2(\mu\text{-}O)]$ [25]. In the basal plane, the average Ti–$O_{phenoxo}$ and Ti–N_{imino} bond lengths are 1.854 and 2.138 Å, respectively, comparable with those previously reported complexes containing (salen)Ti species. The average bond of Ti–$O_{(Ti)}$ (1.815 Å) is significantly shorter than that of Ti–$O_{(ReO4)}$ (2.122 Å), which could be attituded to the stronger competitive π-bonding of the Ti^{VI} with O atom from bridged-oxo of Ti–O–Ti than that with O from ReO_4^-. The bond angle of Ti–O–Ti (168.9°) is more linear than that of Ti–O–Re (147.6°). The rhenium atoms are pseudotetrahedral and are surrounded by three terminal oxygens and one oxygen bonded to the titanium atom. The Re–$O_{bridging}$ distances of (1.738(4)–1.776(5) Å) are longer than that of Re–$O_{terminal}$ (1.680(7)–1.719(6) Å). The O–Re–O angles vary from 107.9(2) to 111.3(2)°. The average Ti$\cdots$Re separation in **2** is 3.780 Å. The bond distances and angles around the Re atoms are very similar to those of bimetallic complexes containing coordinated ReO_4^- group [9–21].

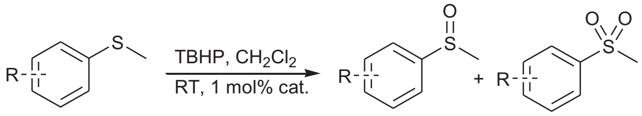
The catalytic activity of Ti^{IV}/Re^{VII} complex **1** was examined using methyl phenyl sulfide as a representative substrate under different reaction conditions. Variations in catalyst loading, oxidants, reaction times and solvents are summarized in Table 3. Among the solvents examined, the optical yield showed a remarkable solvent dependence (entry 1–4). CH_2Cl_2 seemed to be suitable for the reaction. The yield of sulfoxide did not significantly rise with an increase of the loading of catalyst (entry 4,5). Thus, 1 mol% of catalyst loading was chosen. The reaction provided an excellent selectivity when the oxidant was cumene hydroperoxide, whereas more catalyst loading (2.5 mol%) and longer reaction time

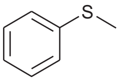
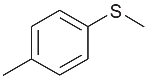
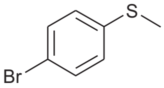
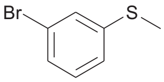
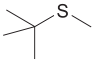
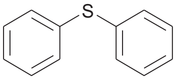
Table 3
Catalytic oxidation of methyl phenyl sulfide.[a]

Entry	Catalyst	Catalyst loading (mol%)	Oxidant	Time (h)	Solvent	Sulfoxide (%)[b]	Sulfone (%)[b]
1	1	1	TBHP	1	CH_3CH_2OH	20	5
2	1	1	TBHP	1	THF	25	7
3	1	1	TBHP	1	$C_6H_5CH_3$	22	4
4	1	1	TBHP	1	CH_2Cl_2	52	16
5	1	5	TBHP	1	CH_2Cl_2	67	20
6	1	2.5	CHP	2	CH_2Cl_2	59	1
7	$[(salen)TiCl_2]$	2.5	TBHP	2	CH_2Cl_2	2	Trace
8	$[\{(salen)TiCl\}_2(\mu\text{-}O)]$	2.5	TBHP	2	CH_2Cl_2	3	Trace
9[c]	$[\{(salen')TiCl\}_2(\mu\text{-}O)]$	4.5	TBHP	144	CH_2Cl_2	61	Trace
10	$[^nBu_4N][ReO_4]$	5	TBHP	3	CH_2Cl_2	2	Trace

[a] Reaction conditions: 0.1 mmol methyl phenyl sulfide, 2 mL solvent, room temperature, TBHP = *t*-butyl hydroperoxide, CHP = cumene hydroperoxide.
[b] Determined by GC.
[c] Ref. [26], salen′ = (R,R′)-*N*,*N*′-(disalicylidene)cyclohexane-1,2-diamine dianion.

Table 4
Oxidation of various sulfide catalyzed by complexes **1** and **2**.[a]



	Substrate	Yield (%)[b]		
		Sulfoxide	Sulfone	
1		77	22	(**1**)
		74	25	(**2**)
2		66	17	(**1**)
		62	15	(**2**)
3		72	27	(**1**)
		80	19	(**2**)
4		63	20	(**1**)
		64	22	(**2**)
5		55	12	(**1**)
		59	15	(**2**)
6		57	18	(**1**)
		49	14	(**2**)

[a] Reaction condition: N_2 atmosphere, 0.1 mmol sulfide, 0.5 mmol TBHP, 1.0 mol% catalyst, 2 mL CH_2Cl_2, room temperature; reaction time 2 h.

[b] Determined by GC.

(2 h) were needed (entry 6). So, the ^{t}BuOOH was the more efficient oxidant reagent for this reaction.

With the reaction conditions established, the scope of substrates of oxidation in this catalytic system was examined. Phenyl sulfides were investigated with TBHP (5 equiv) and 1 mol% of catalyst in CH_2Cl_2 (2 mL). The results are shown in Table 4. It was found that complexes **1** and **2** have the similar reactivity and selectivity for the reactions. All of aryl methyl sulfides, *para*-methyl-, bromo-phenyl methyl sulfides were efficiently converted to the corresponding sulfoxide and sulfone with high yields (Table 4, entries 1–4). The conversion of diphenyl and *t*-butylmethyl sulfide proceeded considerably slower, typically completed in more than 2 h under same conditions (Table 4, entries 5–6). Interestingly, [(salen)TiCl2], $[\{(salen)TiCl\}_2(\mu\text{-}O)]$ and $[^{n}BuN][ReO_4]$ are not active catalysts for the sulfide oxidation (Table 3). So, it suggests that the coordinated ReO_4 group in complexes **1** and **2** should be the potential active component in the catalytic procedure. Lewis acid Ti^{IV} center coordinates ReO_4^- to form $(Ti^{IV}–O)–Re^{VII}O_3$ species, which include ReO_3 fragment as in methyl trioxorhenium (MTO). It is noted that MTO and its derivatives are typical powerful oxidation catalyst with H_2O_2 as the reagent [27–29]. So, presumably Re peroxo species as the reactive intermediates are involved in the Ti^{IV}/Re^{VII} catalyst system. None of sulfoxide products with enantioselectivity are observed.

4. Conclusion

In summary, we have shown that replacement of the chloride ligand in the complexes $[(salen)TiCl_2]$ and $[\{(salen)TiCl\}_2(\mu\text{-}O)]$ by the perrhenate group generates heteropolymetallic complexes **1** and **2**. Structural studies indicate Lewis acid Ti^{IV} center coordinates ReO_4^- to form $(Ti^{IV}–O)–Re^{VII}O_3$ species, which include ReO_3 fragment as in methyl trioxorhenium (MTO). The resulting Ti^{IV}/Re^{VII} complexes can efficiently catalyze oxidation of sulfides with ^{t}BuOOH. Presumably, Re peroxo species as the reactive intermediates are involved in the Ti^{IV}/Re^{VII} catalyst system.

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Appendix A. Supplementary material

UV data of complexes **1** and **2**; Crystallographic data for **2**, which has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 903068. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.12.020.

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